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Multilayer relaxation of a clean bcc Fe{111} surface

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A multilayer low-energy electron diffraction analysis of the Fe{111} surface structure has determined four interlayer spacings. This analysis is a refinement of an earlier analysis that used the same experimental data, but considered only variations of the first interlayer spacing. The first interlayer spacing shows a small increased contraction, but substantial changes are found in the deeper spacings. The optimized structure is (with d_{ik} the spacing between ith and kth atomic layer) $\Delta d_{12} = (-16.9 \pm 3.0)\%$, $\Delta d_{23} = (-9.8 \pm 3.0)\%$, $\Delta d_{34} = (4.2 \pm 3.6)\%$, and $\Delta d_{45} = (-2.2 \pm 3.6)\%$, relative to the bulk spacing of 0.827 Å.

I. INTRODUCTION

The occurrence of multilayer relaxation of the outer layers of metal crystals is now well established.[1] About ten cases have been studied by low-energy electron diffraction (LEED) and ion scattering. In particular, the study of six surfaces of Fe has shown that the relative contraction of the first layer spacing d_{12} increases smoothly with the openness or roughness of the surface and that relaxations go several layers deep.[2] The original work in the Fe{111} surface,[3] which was studied along with the other low-index surfaces {100} and {110} and varied only d_{12}, found the surprisingly large contraction of $(15.4 \pm 3)\%$. However, now that the dependence on openness is known, this result for the (111) surface, a rather open surface, no longer appears as anomalous. What appears to be missing is a study of the changes in deeper interlayer spacings, particularly because open (i.e., loosely packed) metal surfaces are now known to exhibit large multilayer relaxations.[2] Of interest is also the question about what change would be found in the magnitude of d_{12} when multilayer relaxation would be allowed. Thus, we have made a new study of the Fe{111} surface taking into account changes in the first four interlayer spacings. The results show that such an analysis is necessary, since substantial relaxation of deeper layers occur. Also, since the early work was done, the theory of relaxation of metal surfaces has advanced to the status of first-principles calculations[4] which predict the sequence of multilayer relaxations. These predictions are based on total-energy self-consistent calculations which relax layer positions as well as the electron distribution. Hence the present relaxation results provide a valuable test of those theories.[5]

II. ANALYSIS

The experimental data base of 14 nondegenerate LEED spectra at two angles of incidence used in the previous Fe{111} analysis[3] has been reanalyzed using as adjustable parameters the first four interlayer spacings, d_{12}, d_{23}, d_{34}, and d_{45} and the real part of the inner potential V_0. Theoretical spectra were calculated with the same computer programs and scattering potential used for previous iron studies.[6] The imaginary part of the inner potential was fixed at 4 eV, and up to 55 beams were used to represent the wave function between layers. The agreement between experimental and calculated spectra was evaluated quantitatively with the numerical r factor of Zanazzi and Jona.[7]

The method used to optimize the structural and nonstruc-

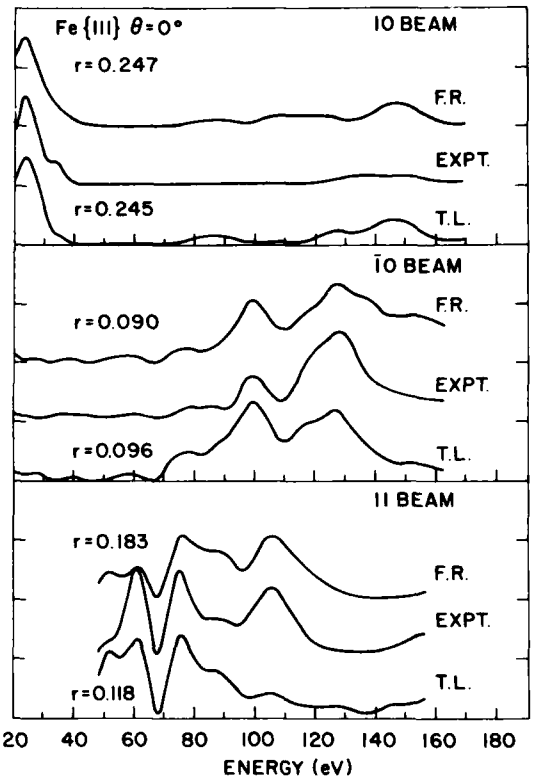

FIG. 1. Experimental and theoretical LEED spectra for Fe{111}, for 10, $\bar{1}$0, and 11 beams at $\theta = 0°$. EXPT. = experiment; F.R. = fully relaxed structure; T.L. = top-layer relaxation only.

tural variables was described previously.[8] Briefly, the optimization was done as follows. (1) A series of calculations involving independent variations of all the structural parameters by relatively large amounts were done in order to get a rough approximation of the optimum structure. For all calculations, the value of the real part of the inner potential V_0 was allowed to vary independently and a minimum r factor was found. (2) All but two of the structural parameters were fixed at the crude "best" values found in (1) and the remaining two structural variables were allowed to vary independently until a minimum of the reliability factor was found. With the refined values of these two parameters thus obtained, a new pair of variables was chosen and the process repeated. The pairs considered were (d_{12},d_{23}), (d_{23},d_{34}), and (d_{34},d_{45}); when the consistency among optimum values determined for members of different pairs was within the estimated experimental uncertainties (3%–4% of an interlayer spacing), the analysis was terminated. In addition, variation of the angle of incidence away from the nominal experimental value of 9° (measured on the sample goniometer) was considered and an optimum value of 8° was obtained. The results of the analysis were as follows:

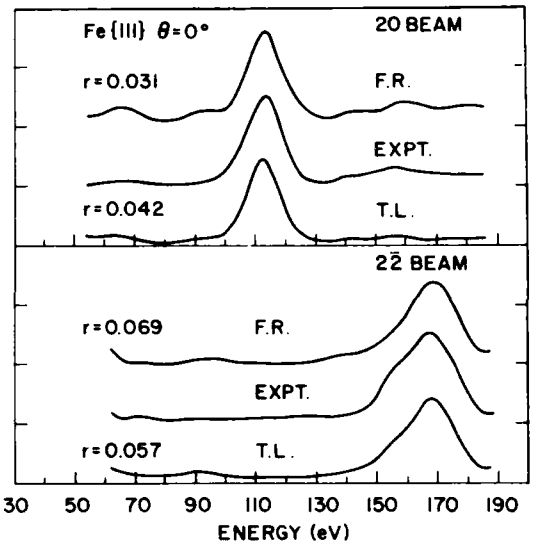

FIG. 2. Experimental and theoretical LEED spectra for Fe{111}, for 20 and 2$\bar{2}$ beams at $\theta=0°$. EXPT. = experiment; F.R. = fully relaxed structure; T.L. = top-layer relaxation only.

$d_{12}=0.69\pm0.025$ Å [(-16.9 ± 3.0)% contraction relative to bulk value of 0.827 Å],

$d_{23}=0.75\pm0.025$ Å [(-9.8 ± 3.0)% contraction],

$d_{34}=0.86\pm0.03$ Å [$(+4.2\pm3.6)$% expansion],

$d_{45}=0.81\pm0.03$ Å [(-2.2 ± 3.6)% contraction],

$V_{0r}=-12.6\pm1.0$ eV (real part of the inner potential),

$r_{\min}=0.131$

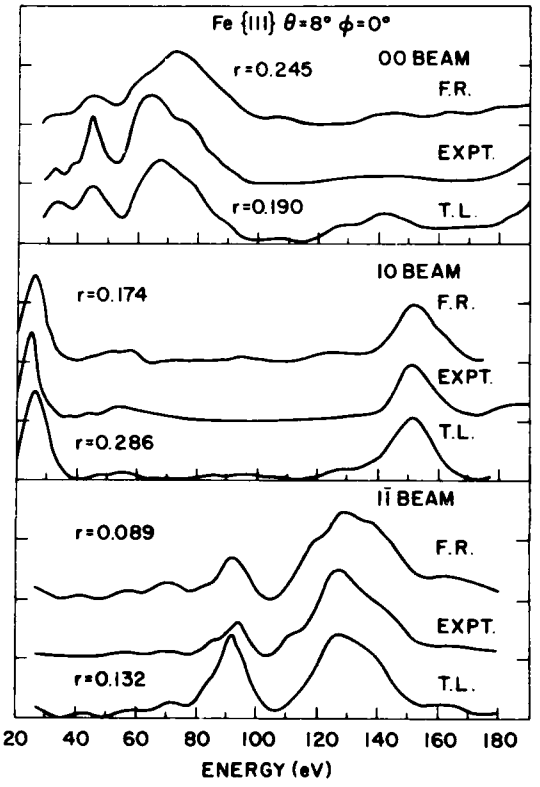

FIG. 3. Experimental and theoretical LEED spectra for Fe{111}, for 00, 10, and 1$\bar{1}$ beams at $\theta=8°$, $\phi=0°$. EXPT. = experiment; F.R. = fully relaxed structure; T.L. = top-layer relaxation only.

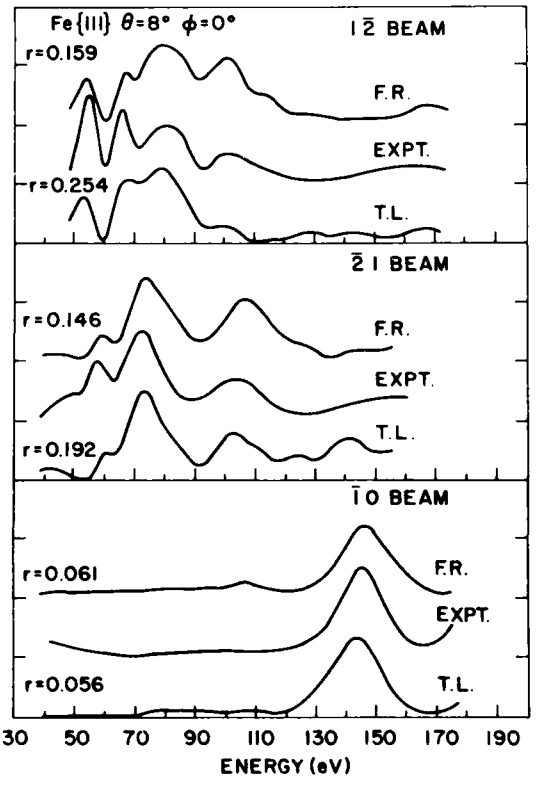

FIG. 4. Experimental and theoretical LEED spectra for Fe{111}, for 1$\bar{2}$, $\bar{2}$1, and $\bar{1}$0 beams at $\theta=8°$, $\phi=0°$. EXPT. = experiment; F.R. = fully relaxed structure; T.L. = top-layer relaxation only.

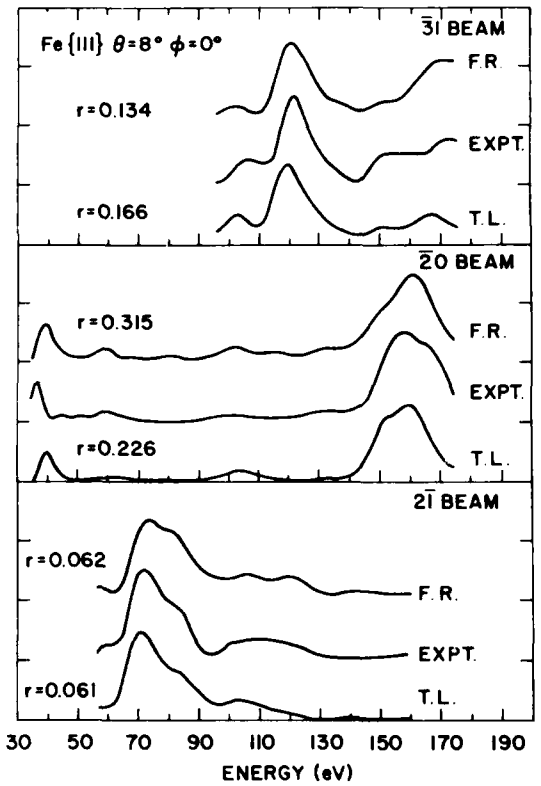

FIG. 5. Experimental and theoretical LEED spectra for Fe{111}, for $\bar{3}1$, $\bar{2}0$, and $2\bar{1}$ beams at $\theta = 8°$, $\phi = 0°$. EXPT. = experiment; F.R. = fully relaxed structure; T.L. = top-layer relaxation only.

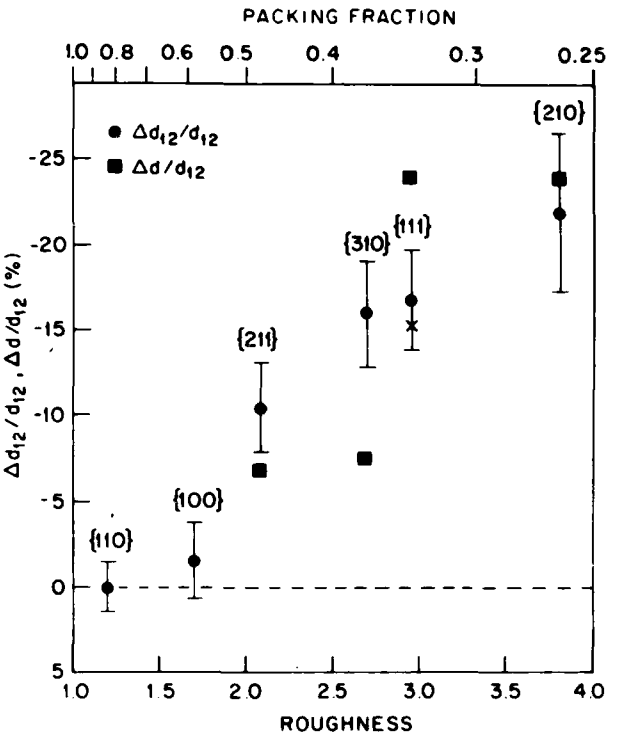

FIG. 6. Top-layer relaxation of Fe surfaces relative to bulk spacing in percent vs surface roughness (inverse of packing fraction). The cross is the result obtained when the relaxation of the top layer is the only relaxation allowed (Ref. 3); the circle is the result obtained with the refinement done in the present work. The squares give $\Delta d/d_{12}$, the total relaxation of the top layer (Ref. 9) relative to bulk spacing in percent.

(r_{min} is the minimum of the Zanazzi-Jona r factor for the data base of 14 beams; the value obtained when only variation of the first interlayer spacing is considered is 0.156).

Figures 1–5 show the comparison between experimental and theoretical LEED spectra for both the fully relaxed model and the optimum model obtained when only top-layer relaxation was considered.[3] Figure 6 shows a plot of top-layer surface relaxation versus surface roughness or packing fraction (top scale) for six iron surfaces.[2] In Fig. 6, the cross and the circle for the {111} surface indicate the optimum values for top-layer relaxation found when considering top-layer relaxation only and multilayer relaxation, respectively. The squares give the relative total relaxation[9] of the first layer for the surfaces with multilayer relaxation.

III. CONCLUSION

The multilayer analysis has increased the relative contraction of d_{12} to 16.9% and revealed a large contraction of d_{23}, which, combined with changes in d_{34} and d_{45}, gives a total relaxation Δd of the first layer with respect to bulk of -0.20 Å, the largest value of the six iron surfaces investigated to date ($\Delta d = -0.08$ Å {211}, -0.07 Å {310}, -0.15 Å {210}), and about the same relative total contraction as {210} ($\Delta d/d_{12} = -6.8\%$ {211}, -7.5% {310}, -24% {210}, -24% {111}). The sequence of changes in layer spacings (contraction, contraction, expansion, contraction) is the same as for the {210} surface, whereas the {211} and {310} surfaces show strict alternation of sign. Determination of the signs and magnitudes of relaxations on these various surfaces provides good quantitative data to test metal surface theory. The new multilayer parameters for Fe{111} offer the unique combination of a surface that is both strongly relaxed and highly symmetric, without the complication of parallel relaxation.[10]

ACKNOWLEDGMENTS

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[2]J. Sokolov, F. Jona, and P. M. Marcus, Solid State Commun. **49**, 507 (1984). The openness or roughness of the surface is defined as the inverse of the packing fraction, which is the fraction of the layer area occupied by atoms having the touching radii of bulk atoms.

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[4]Al{110} multilayer relaxation has been studied by K. M. Ho and

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[5]A calculation for Fe surfaces should be carried out with the spin-polarized formulation of self-consistent band theory, which has been applied to bulk crystals, but was not used in the calculations of Ref. 4.

[6]J. Sokolov, H. D. Shih, U. Bardi, F. Jona, and P. M. Marcus, J. Phys. C **17**, 371 (1983).

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[8]J. Sokolov, F. Jona, and P. M. Marcus, Phys. Rev. B **31**, 1929 (1985).

[9]The total relaxation $\Delta d = \Delta d_{12} + \Delta d_{23} + \Delta d_{34} + \Delta d_{45} + \cdots$ gives the total perpendicular movement of the first layer with respect to its position for a truncated bulk lattice. The relative value is obtained by dividing by the bulk interlayer spacing.

[10]No first-principles study of the relaxation of bcc {111} surfaces seems to have been made yet. R. N. Barnett, U. Landman, and C. L. Cleveland, Phys. Rev. B **27**, 6534 (1983), study a number of simple models by total-energy minimization. They consider Na{111} and for some models, including their most realistic one (which includes dipole-layer, Hartree, and band-structure energy contributions), they find the same sequence of signs of the relaxations as found here.